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[Claim(s)]

[Claim 1]A negative electrode plate and a cathode board which uses $LiNi_xM_{1-x}O_2$ (M is any one or more kinds of Co, Mn, Cr, Fe, V, and aluminum, and x:1>x>=0.5) as positive active material, In a nonaqueous electrolyte battery which passes a separator between said negative electrode plate and a cathode board, Minute-crystals grains which have said positive active material in a range whose unidirectional particle diameter (Feret diameter) in SEM observation is 0.1-2 micrometers, A nonaqueous electrolyte battery which consists of a mixture with an aggregated particle where said a majority of minute-crystals grains gather, and which is in a range whose unidirectional particle diameter (Feret diameter) is 2-20 micrometers.

[Claim 2]an aggregated particle -- shape -- a globular shape or an ellipse -- the spherical nonaqueous electrolyte battery according to claim 1.

[Claim 3]The nonaqueous electrolyte battery according to claim 1 whose mixing ratio over an aggregated particle of minute-crystals grains is 5 to 50% of range in a weight ratio.

[Claim 4]The nonaqueous electrolyte battery according to claim 1 with which minute-crystals grains grind an aggregated particle.

[Claim 5]positive-active-material $LiNi_xM_{1-x}O_2$ (M -- Co and Mn.) It is one or more kinds chosen from among Cr, Fe, V, and aluminum, and is a manufacturing method of x:1>x>=0.5, Many minute-crystals grains whose unidirectional particle diameter (Feret diameter) in SEM observation is 0.1-2 micrometers are aggregated particles which gathered, $nickel_xM_{1-x}(OH)_2$ in a range whose unidirectional particle diameter of this aggregated particle is 2-20 micrometers () [M] [Co and] A manufacturing method of positive active material for nonaqueous electrolyte batteries which is chosen from among Mn, Cr, Fe, V, and aluminum and which is one or more kinds, mixes x:1>x>=0.5 with lithium carbonate or lithium hydroxide, heat-treats this mixture, and obtains positive active material.

[Claim 6]an aggregated particle -- shape -- a globular shape or an ellipse -- a manufacturing method of the spherical positive active material for nonaqueous electrolyte batteries according to claim 5.

[Claim 7]positive-active-material $LiNi_xM_{1-x}O_2$ (M -- Co and Mn.) It is one or more kinds chosen from among Cr, Fe, V, and aluminum, and is a manufacturing method of x:1>x>=0.5, $nickel_xM_{1-x}(OH)_2$ (M -- Co and Mn --) [Cr, Fe and] Are one or more kinds chosen from among V and aluminum, and it is expressed with x:1>x>=0.5, A part of aggregated particle in a range whose unidirectional particle diameter in which many minute-crystals grains whose unidirectional particle diameter (Feret diameter) in SEM observation is 0.1-2 micrometers gathered is 2-20 micrometers is ground to said minute-crystals grain, A manufacturing method of positive active material for

nonaqueous electrolyte batteries which is mixed with lithium carbonate or lithium hydroxide, heat-treats these mixtures, and obtains positive active material after mixing this grinding thing with said aggregated particle of a non-crushing condition.
[Claim 8]A manufacturing method of the positive active material for nonaqueous electrolyte batteries according to claim 7 whose mixing ratio over an unground thing of an aggregated particle of a grinding thing of an aggregated particle is 5 to 50% of range in a weight ratio.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of a nonaqueous electrolyte secondary battery and its positive active material.
It is related especially with the battery characteristic improvement.

[0002]
[Description of the Prior Art]In recent years, portable-izing of consumer electronics and cordless-ization are progressing rapidly. Although the nickel cadmium battery or the closed mold small lead storage battery is bearing a role of a power supply for a drive of these electronic equipment now, The request of high-energy-density-izing of the secondary battery used as the power supply for a drive and a small weight saving is strong as portable-izing and cordless-ization are progressed and established.
[0003]It is observed as a power supply for cellular phones, and the request to protraction of duration of a call and an improvement of a cycle life is very large with expansion of the rapid commercial scene in recent years.
[0004]The lithium compound transition metal oxide (for example, JP,63-59507,A gazette), for example, $LiCoO_2$, which show high charge and discharge voltage from such a situation, $LiNiO_2$ which furthermore aimed at high capacity (for example, US,4302518,B), two or more metallic elements and the multiple oxide (for example, $LiyNixCo1\text{-}xO_2$: JP,S63-299056,A, $LixMyNzO_2$ (however, M was chosen from Fe, Co, and nickel -- it being a kind at least and)) of lithium As for N, the nonaqueous electrolyte secondary battery selected from Ti, V, Cr, and Mn which used kind:JP,H43-267053,A for positive active material at least, and used intercalation of a lithium ion and secession is proposed.
[0005]moreover -- the physical properties of positive active material -- mean particle diameter (JP,H1-304664,A.) The improving method about JP,H6-243897,A, JP,H6-290783,A, JP,H7-114942,A, or shape (JP,H6-267539,A, JP,H7-37576,A) is proposed.
[0006]
[Problem to be solved by the invention]However, in the nonaqueous electrolyte secondary battery which used for positive active material $LiNiO_2$ reported until now, the problem of cycle degradation that the battery discharge capacity decreased gradually became whether to be ** by carrying out by repeating a charging and discharging cycle.
[0007]As a result of this invention persons' repeating examination enough, it turned out that the following [characteristic degradation / such] is the cause.
[0008]As a result of disassembling the cell which carried out cycle degradation and conducting the X-ray analysis of a polar plate, in the cathode board which repeated the charging and discharging cycle, it became clear that the crystal structure of positive active material was changing remarkably.

[0009]As for $LiNiO_2$, it is reported in connection with the charge and discharge of a cell that the grating constant changes, (S. Yamada, M.Fujiwara and M.Kanda, J. Power Source, 54,209 (1995)) It is known that a axis and c axis of expansion contraction are large.

[0010]Thus, by repeating a charging and discharging cycle, the active material expanded and contracted, omission from amorphous-izing of crystal structure, the miniaturization of grains, and the polar plate of an active material arose, and that it is because the amount of active materials which can participate in charge and discharge decreased became whether to be **.

[0011]When it was the lithium containing compound metal oxide which substituted some nickel by other metal to such SUBJECT, change of crystal structure was eased and the good cycle characteristic was shown.

[0012]However, while the cycle characteristic improved, discharge capacity became small, and the active material which substituted some nickel by other metallic elements in this way had a problem to which discharge capacity falls remarkably at the time of the high rate discharge through which discharge potential sends especially a high current by becoming low.

[0013]In order to raise a high rate discharging characteristic, when atomization of the active material was considered, there was a problem to which the restoration nature to a cell plate falls to remarkably, and the cell capacity itself falls.

[0014]The purpose of this invention is to provide the nonaqueous electrolyte secondary battery which was excellent in the charging and discharging characteristic by aiming at solution of the problem about the above-mentioned conventional cathode, providing better positive active material and using the grain size of specific positive active material, particle shape, and a filling method.

[0015]

[Means for solving problem]In order to solve such a problem, we substituted some nickel of $LiNiO_2$ by other metallic elements, and we examined further wholeheartedly the filling method of the size of the grains of positive active material, shape, and the active material at the time of polar plate composition. As a result, by controlling these factors, it is high capacity and comes to realize a cell with good cycle characteristic and high rate discharging characteristic.

[0016]This invention uses $LiNi_xM_{1-x}O_2$ (M is any one or more kinds of Co, Mn, Cr, Fe, V, and aluminum, and x:1>x>=0.5) as positive active material, and concretely. [this invention] The minute grain child who has this positive active material in the range whose unidirectional particle diameter (Feret diameter) in SEM observation is 0.1-2 micrometers, It is a thing using the thing which mixed the aggregated particle in the range whose unidirectional particle diameter (Feret diameter) in which many minute-crystals grains gather is 2-20 micrometers as positive active material.

[0017]an aggregated particle -- a globular shape or an ellipse -- a spherical thing is desirable and, as for the mixing ratio of the minute-crystals grains to mix, it is desirable that it is 5 to 50% of range in a weight ratio.

[0018]nickel$_xM_{1-x}(OH)_2$ (M -- Co, Mn, Cr, Fe, and V.) which has such a spherical active material in the range whose unidirectional particle diameter in which many minute-crystals grains whose unidirectional particle diameter (Feretdiameter) in SEM observation is 0.1-2 micrometers as a raw material gathered is 2-20 micrometers Lithium salt (either lithium carbonate or lithium hydroxide) can be mixed with any one or more kinds of aluminum, and x:1>x>=0.5, and it can obtain by heat-treating this mixture.

[0019]Positive-active-material $LiNi_xM_{1-x}O_2$ which compounded the minute-crystals grains to mix () [M] [Co and] . [grind / any one or more kinds of Mn, Cr, Fe, V, and aluminum and x:1>x>=0.5] Or raw material nickel$_xM_{1-x}(OH)_2$ ground beforehand () [M] [Co and] After mixing any one or more kinds of Mn, Cr, Fe, V, and aluminum, and x:1>x>=0.5 with an aggregated particle, it can mix with lithium salt (either lithium carbonate or

lithium hydroxide), and can obtain also by heat-treating this mixture.

[0020]The unidirectional particle diameter (Feret diameter) in SEM observation is adopted as a measuring method of particle diameter, and this is the thing which read in a certain certain direction the path of the grains which turned to various directions in the SEM photograph, and averaged it. (Reference documents: Basic p.285 (edited by Nikkan Kogyo Shimbun) of fine-particles engineering)

[0021]

[Mode for carrying out the invention]When the positive active material by this invention is used, the unidirectional particle diameter in SEM observation enlarges the contact area of positive-active-material grains and an electrolyte, when 0.1-2 micrometers and a very small minute grain child use the positive active material which is a primary particle, Improve reduction of the interface concentration of the Li ion which was the cause of increase of polarization at the time of high rate discharge, and. The space part produced between aggregated particles by mixing an aggregated particle and minute-crystals grains is filled up with minute-crystals grains, and the electric conductivity between grains is raised, and it becomes possible to improve remarkably the restoration nature of the active material in a polar plate.

[0022]The key map of the positive active material in this invention was shown in drawing 1. If the method of this invention is used, when the positive active material of this invention will be measured, for example using a laser particle-size-distribution meter, it turns out that particle size distribution has two peaks.

[0023]Needless to say, the grains of a side with a large grain size of these two peaks are the grain sizes of an aggregated particle, and the peak of a side with a small grain size is a detailed grain child's added grain size.

[0024]Such an effect is not acquired only by limiting the shape of an active material, and a grain size, for example like JP,H6-267539,A, JP,H1-304664,A, JP,H6-243897,A, and JP,H7-37576,A.

[0025]

[Work example 1]Hereafter, the embodiment of this invention is described, making Drawings reference.

[0026]The longitudinal section of the cylinder system cell used by this example 1 is shown in drawing 2. The cell case into which 1 processed the stainless steel plate of organic electrolysis-proof acidity or alkalinity in drawing 2, the obturation board with which 2 provided the safety valve, and 3 show insulating packing. 4 is a group of electrode, and the cathode board 5 and the negative electrode plate 6 are spirally wound two or more times via the separator 7, and it is stored in the case. And from the above-mentioned cathode board 5, the cathode aluminum lead 5a is pulled out and it is connected to the obturation board 2, and from the negative electrode plate 6, the anode nickel lead 6a is pulled out and it is connected to the bottom of the cell case 1. 8 is provided in the vertical section of the group of electrode 4 with the insulating ring, respectively.

[0027]Hereafter, the negative electrode plate 6, an electrolyte, etc. are explained in detail. The negative electrode plate 6 mixed the styrene butadiene system binder to carbon powder 100 weight section which heat-treated corks, made the carboxymethylcellulose aqueous solution suspended in it, and was made into paste state at it. And the surface of 0.015-mm-thick copper foil was plastered with this paste, and a negative electrode plate after-desiccation 0.2 mm in thickness, 37 mm in width, and 300 mm in length was created.

[0028]Hereafter, the synthetic process of positive active material is explained in detail. The sodium hydroxide solution was added having introduced the nickel sulfate solution and the cobalt sulfate solution in the container, and agitating them enough with constant flow, using nickel sulfate, cobalt sulfate, and a sodium hydroxide solution.

[0029]Nickel cobalt compound hydroxide with various grain sizes was obtained by changing the addition of sodium hydroxide.

[0030]The nickel cobalt compound hydroxide which washes the generated settlings, dries and has various grain sizes was obtained.

[0031]All the chemical composition of the obtained nickel cobalt compound hydroxide was $nickel_{0.85}Co_{0.15}(OH)_2$.

[0032]The nickel cobalt compound hydroxide created by the method of this example is a spherical aggregated particle in which many minute grain children (primary particle) in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle diameter from a SEM photograph.
The unidirectional particle diameter of the aggregated particle was 0.5, 2.0, 5.0 and 10, and 20 or 30 micrometers, respectively.

[0033]The obtained nickel cobalt compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Co_{0.15}O_2$ was compounded.

[0034]The SEM photograph of the obtained lithium compound nickel cobalt oxide is shown in drawing 3. [the compounded lithium compound nickel cobalt oxide] It is obtained as a spherical aggregated particle whose unidirectional particle diameter in which many minute grain children in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 0.51, 2.53, 5.04 and 10.1, and 20.7 or 30.5 micrometers, respectively, The shape of nickel cobalt compound hydroxide which is a raw material is maintained mostly.
It was spread inside, without lithium changing the shape of nickel cobalt compound hydroxide at the time of synthesis, and has checked that the reaction was advancing.

[0035]Each lithium compound nickel cobalt oxide obtained by the above synthesizing method was extracted by 0, 5, 20, 50, and 70 or 100% with the wt. ratio, and after the ball mill ground until it became a primary particle, respectively, it mixed with the unground thing.
[0036]By the above method, a total of 36 kinds of positive active material were compounded. Henceforth, the manufacturing method of a cathode board is explained.
[0037]A cathode board mixes acetylene black 3 weight section and fluororesin system binder 5 weight section to powder 100 weight section of $LiNi_{0.85}Co_{0.15}O_2$ which is positive active material first, makes N-methyl-pyrrolidone solution suspended in it, and is made into paste state at it. Both sides of 0.020-mm-thick aluminum foil were plastered with this paste, and the cathode board 5 after-desiccation 0.130 mm in thickness, 35 mm in width, and 270 mm in length was created.
[0038]And a cathode board and a negative electrode plate were spirally stored via a separator in a cell case winding, 13.8 mm in diameter, and 50 mm in height.
[0039]After pouring into the group of electrode 4 using what was dissolved in ethylene carbonate and an isochore product mixed solvent of ethyl carbonate methyl at a rate of 1 mol/l. of lithium hexafluorophosphate, the seal mouth of the cell was carried out to an electrolyte, and it was made it with a testing cell.
[0040]A testing cell number applicable to each positive active material made as an experiment by this example 1 to (Table 1) was written.
[0041]
[Table 1]

粉砕物混合重量比	LiNiCoO$_2$二次粒子径（μm）					
	0.5	2.5	5.0	10	20	30
0	1	7	13	19	25	31
5	2	8	14	20	26	32
20	3	9	15	21	27	33
50	4	10	16	22	28	34
70	5	11	17	23	29	35
100	6	12	18	24	30	36

[0042]
[Work example 2]As the 2nd embodiment, nickel manganese compound hydroxide was generated like Embodiment 1, using nickel sulfate, manganese sulfate, and a sodium hydroxide solution as a salt water solution which manufactures nickel manganese compound hydroxide.
[0043]The obtained nickel manganese compound hydroxide is a spherical aggregated particle in which many minute grain children in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle diameter from a SEM photograph.
The unidirectional particle diameter of the aggregated particle was 5.0 micrometers.

[0044]The obtained nickel manganese compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Mn_{0.15}O_2$ was compounded.
[0045]The spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have the compounded lithium compound nickel manganic acid ghost in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 5.2 micrometers, respectively was obtained.
[0046]After the ball mill ground until it extracted the lithium compound nickel manganic acid ghost obtained by the above synthesizing method by 20% with the wt. ratio and became a primary particle, it mixed with the unground thing, and was considered as positive active material, and the cell was created like Embodiment 1. The cell in the above-mentioned Embodiment 2 was used as the cell 37.
[0047]
[Work example 3]As the 3rd embodiment, nickel chromium compound hydroxide was generated like Embodiment 1, using nickel sulfate, chromium sulfate, and a sodium hydroxide solution as a salt water solution which manufactures nickel chromium compound hydroxide.
[0048]The obtained nickel chromium compound hydroxide is a spherical aggregated particle in which many minute grain children in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle

diameter from a SEM photograph.
The unidirectional particle diameter of the aggregated particle was 5.0 micrometers.

[0049]The obtained nickel chromium compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Cr_{0.15}O_2$ was compounded.

[0050]The spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have the compounded lithium compound nickel chromium oxidation thing in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 5.4 micrometers, respectively was obtained.
[0051]After the ball mill ground until it extracted the lithium compound nickel chromium oxidation thing obtained by the above synthesizing method by 20% with the wt. ratio and became a primary particle, it mixed with the unground thing, and was considered as positive active material, and the cell was created like Embodiment 1. The cell in the above-mentioned Embodiment 3 was used as the cell 38.
[0052]
[Work example 4]As the 4th embodiment, ferronickel compound hydroxide was generated like Embodiment 1, using nickel sulfate, iron sulfate, and a sodium hydroxide solution as a salt water solution which manufactures ferronickel compound hydroxide.
[0053]The obtained ferronickel compound hydroxide is a spherical aggregated particle in which many minute grain children in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle diameter from a SEM photograph.
The unidirectional particle diameter of the aggregated particle was 5.0 micrometers.

[0054]The obtained ferronickel compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Fe_{0.15}O_2$ was compounded.

[0055]The spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have the compounded lithium compound ferronickel oxide in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 4.9 micrometers, respectively was obtained.
[0056]After the ball mill ground until it extracted the lithium compound ferronickel oxide obtained by the above synthesizing method by 20% with the wt. ratio and became a primary particle, it mixed with the unground thing, and was considered as positive active material, and the cell was created like Embodiment 1. The cell in the above-mentioned Embodiment 4 was used as the cell 39.
[0057]
[Work example 5]As the 5th embodiment, nickel vanadium compound hydroxide was generated like Embodiment 1, using nickel sulfate, vanadium sulfate, and a sodium hydroxide solution as a salt water solution which manufactures nickel vanadium compound hydroxide.
[0058]The obtained nickel vanadium compound hydroxide is a spherical aggregated particle in which many minute grain children in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle diameter from a SEM photograph.
The unidirectional particle diameter of the aggregated particle was 4.8 micrometers.

[0059]The obtained nickel vanadium compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}V_{0.15}O_2$ was compounded.

[0060]The spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have the compounded lithium compound nickel vanadium oxide in the range whose unidirectional

particle diameter in SEM observation is 0.1-2 micrometers gather is 5.5 micrometers, respectively was obtained.
[0061]After the ball mill ground until it extracted the lithium compound nickel vanadium oxide obtained by the above synthesizing method by 20% with the wt. ratio and became a primary particle, it mixed with the unground thing, and was considered as positive active material, and the cell was created like Embodiment 1. The cell in the above-mentioned Embodiment 5 was used as the cell 40.
[0062]
[Work example 6]As the 6th embodiment, nickel aluminium compound hydroxide was generated like Embodiment 1, using nickel sulfate, aluminium sulfate, and a sodium hydroxide solution as a salt water solution which manufactures nickel aluminium compound hydroxide.
[0063]The obtained nickel aluminium compound hydroxide is a spherical aggregated particle in which many minute grain children in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle diameter from a SEM photograph.
The unidirectional particle diameter of the aggregated particle was 4.3 micrometers.

[0064]The obtained nickel aluminium compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}aluminum_{0.15}O_2$ was compounded.
[0065]The spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have the compounded lithium compound nickel aluminum oxide in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 4.4 micrometers, respectively was obtained.
[0066]Lithium compound nickel ARUMINIMU obtained by the above synthesizing method After the ball mill ground until it extracted the oxide by 20% with the wt. ratio and became a primary particle, it mixed with the unground thing, and was considered as positive active material, and the cell was created like Embodiment 1. The cell in the above-mentioned Embodiment 6 was used as the cell 41.
[0067]
[Work example 7]As the 7th embodiment, nickel cobalt manganese compound hydroxide was generated like Embodiment 1, using nickel sulfate, cobalt sulfate, manganese sulfate, and a sodium hydroxide solution as a salt water solution which manufactures nickel cobalt manganese compound hydroxide.
[0068]Obtained nickel cobalt manganese compound hydroxide is a spherical aggregated particle in which many minute grain children in the range of 0.1-2 micrometers gather as a result of measuring unidirectional particle diameter from a SEM photograph.
Unidirectional particle diameter of an aggregated particle was 5.7 micrometers.

[0069]Obtained nickel cobalt manganese compound hydroxide was mixed with lithium hydroxide, under an oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Co_{0.1}Mn_{0.05}O_2$ was compounded.
[0070]A spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have a compounded lithium compound nickel cobalt manganic acid ghost in a range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 6.3 micrometers, respectively was obtained.
[0071]Each lithium compound nickel cobalt manganic acid ghost obtained by the above synthesizing method is extracted by 0, 5, 20, 50, and 70 or 100% with a wt. ratio, After a ball mill ground until it became a primary particle, respectively, it mixed with an unground thing, and was considered as positive active material, and a cell was created like Embodiment 1. A cell in the above-mentioned Embodiment 7 was set to 42, 43, 44, 45, 46, and 47, respectively.
[0072]
[Work example 8]Nickel cobalt compound hydroxide whose unidirectional particle diameter in SEM observation is

5.1 micrometers was generated by the same method as Embodiment 1, and each was extracted by 0, 5, 20, 50, and 70 or 100% with the wt. ratio, and after the ball mill ground until it became a primary particle, respectively, it mixed with the unground thing.

[0073]The obtained nickel cobalt compound hydroxide was mixed with lithium hydroxide, under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Co_{0.15}O_2$ was compounded.

[0074][the compounded lithium compound nickel cobalt oxide] It is obtained as a mixture of the spherical aggregated particle whose unidirectional particle diameter in which many minute grain children in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 6.04 micrometers, and the minute grain child in the range of 0.1-2 micrometers, The shape of nickel cobalt compound hydroxide which is a raw material is maintained mostly.

It was spread inside, without lithium changing the shape of nickel cobalt compound hydroxide into ******, and has checked that the reaction was advancing.

[0075]Thus, the obtained lithium compound nickel cobalt oxide was used as positive active material, respectively, and also the cell was created like Embodiment 1.

[0076]The cell in the above-mentioned Embodiment 8 was set to 48, 49, 50, 51, 52, and 53, respectively.

[0077]

[Work example 9]Nickel cobalt compound hydroxide whose unidirectional particle diameter in SEM observation is 5.1 micrometers was generated by the same method as Embodiment 1, and it mixed with lithium hydroxide, and under the oxidizing atmosphere, it calcinated at 700 ** for 10 hours, and $LiNi_{0.85}Co_{0.15}O_2$ was compounded.

[0078]The spherical aggregated particle whose unidirectional particle diameter in which many minute grain children who have the compounded lithium compound nickel cobalt oxide in the range whose unidirectional particle diameter in SEM observation is 0.1-2 micrometers gather is 6.04 micrometers was obtained.

[0079]Thus, use the obtained lithium compound nickel cobalt oxide as positive active material, and like Embodiment 1, [powder 100 weight section of $LiNi_{0.85}Co_{0.15}O_2$] Mix acetylene black 3 weight section and fluorine resin system binder 5 weight section, N-methyl-pyrrolidone solution is made suspended, and it is made paste state. It plastered so that the thickness after drying this paste to both sides of 0.020-mm-thick aluminum foil might be set to 0.4 mm, and rolling was repeated until thickness was set to 0.130 mm with the after-desiccation roller press.

[0080]It was checked that about 10% of aggregated particles are ground by the primary particle, and the opening between aggregated particles is filled up with the positive active material of the obtained polar plate by the roller press.

[0081]The obtained cathode board was used and also the cell was created like Embodiment 1. The cell in the above-mentioned Embodiment 9 was used as the cell 54.

[0082]

[Comparative example 1] The lithium compound nickel cobalt oxide was compounded like Embodiment 1 by making into a raw material nickel cobalt compound hydroxide whose unidirectional particle diameter of the aggregated particle in which many minute grain children whose unidirectional particle diameter (Feret diameter) is 5 micrometers gather as the comparative example 1 is 15 micrometers. The chemical composition of the obtained compound was $LiNi_{0.85}Co_{0.15}O_2$.

[0083]The compounded lithium compound nickel cobalt oxide was obtained as a spherical aggregated particle whose unidirectional particle diameter in which many minute grain children whose unidirectional particle diameter in SEM observation is 5.2 micrometers gather is 17 micrometers, respectively.

[0084]Each lithium compound nickel cobalt oxide obtained by the above synthesizing method was extracted by 20% with the wt. ratio, and after the ball mill ground until it became a primary particle, respectively, it mixed with the unground thing.
[0085]The active material obtained by the above-mentioned method was used, and also the cell was created like Embodiment 1. The cell in the above-mentioned comparative example 1 was used as the cell 55.
[0086]
[Comparative example 2] As the comparative example 2, the shape of grains compounded the lithium compound nickel cobalt oxide like Embodiment 1 by making massive nickel cobalt compound hydroxide into a raw material. The chemical composition of the obtained nickel cobalt compound hydroxide was $LiNi_{0.85}Co_{0.15}O_2$.
[0087]The compounded lithium compound nickel cobalt oxide was obtained as massive grains whose unidirectional particle diameter in SEM observation is 16 micrometers.
[0088]It extracted by 20% with the wt. ratio, and after the ball mill ground, respectively, it mixed with the unground thing.
[0089]The lithium compound nickel cobalt oxide obtained by the synthesizing method of the more than obtained by the above-mentioned method was used as positive active material, and also the cell was created like Embodiment 1.
[0090]The cell in the above-mentioned comparative example 2 was used as the cell 56.
[0091]
[Comparative example 3] The lithium compound nickel oxide was compounded like Embodiment 1 by making into a raw material spherical nickel hydroxide whose unidirectional particle diameter of the aggregated particle in which many minute grain children whose unidirectional particle diameter (Feret diameter) is 1 micrometer gather as the comparative example 3 is 15 micrometers. The chemical composition of the obtained lithium compound nickel oxide was $LiNiO_2$.
[0092]The compounded lithium compound nickel oxide was obtained as a spherical aggregated particle whose unidirectional particle diameter in which many minute grain children whose unidirectional particle diameter in SEM observation is 1.2 micrometers gather is 16 micrometers, respectively.
[0093]Each lithium compound nickel oxide obtained by the above synthesizing method was extracted by 20% with the wt. ratio, and after the ball mill ground until it became a primary particle, respectively, it mixed with the unground thing.
[0094]The active material obtained by the above-mentioned method was used, and also the cell was created like Embodiment 1. The cell in the above-mentioned comparative example 1 was used as the cell 57.
[0095]Thus, charge and discharge were repeated at 20 **, the charge final voltage 4.2V, the discharge final voltage 2.5V, and 500 mA, the created cells 1-57 were performed, and the cycle charge and discharge test was done.
[0096]The cycle test result of the cell of the embodiment of this invention and a comparative example is shown in Tables 2-6. It examined by having assembled the 30 cells 1-57, respectively, and the average was shown in Table 2 - (Table 6).
[0097]
[Table 2]

電池	置換元素量	一次粒子径 (μm)	二次粒子径 (μm)	二次粒子形状	微粉混合率 (%)	放電容量 (mAh) 5サイクル	500サイクル
1	Co 15%	0.1～2	0.51	球状	0	385	356
2	Co 15%	0.1～2	0.51	球状	5	442	416
3	Co 15%	0.1～2	0.51	球状	20	450	426
4	Co 15%	0.1～2	0.51	球状	50	420	396
5	Co 15%	0.1～2	0.51	球状	70	405	398
6	Co 15%	0.1～2	0.51	球状	100	395	326
7	Co 15%	0.1～2	2.53	球状	0	502	485
8	Co 15%	0.1～2	2.53	球状	5	596	556
9	Co 15%	0.1～2	2.53	球状	20	605	576
10	Co 15%	0.1～2	2.53	球状	50	550	556
11	Co 15%	0.1～2	2.53	球状	70	550	487
12	Co 15%	0.1～2	2.53	球状	100	405	377
13	Co 15%	0.1～2	5.04	球状	0	531	506
14	Co 15%	0.1～2	5.04	球状	5	605	568
15	Co 15%	0.1～2	5.04	球状	20	620	586
16	Co 15%	0.1～2	5.04	球状	50	595	551
17	Co 15%	0.1～2	5.04	球状	70	535	456
18	Co 15%	0.1～2	5.04	球状	100	445	361
19	Co 15%	0.1～2	10.1	球状	0	495	466
20	Co 15%	0.1～2	10.1	球状	5	608	564
21	Co 15%	0.1～2	10.1	球状	20	618	579
22	Co 15%	0.1～2	10.1	球状	50	601	561
23	Co 15%	0.1～2	10.1	球状	70	542	447
24	Co 15%	0.1～2	10.1	球状	100	437	352
25	Co 15%	0.1～2	20.7	球状	0	483	406
26	Co 15%	0.1～2	20.7	球状	5	592	494
27	Co 15%	0.1～2	20.7	球状	20	602	509
28	Co 15%	0.1～2	20.7	球状	50	595	482
29	Co 15%	0.1～2	20.7	球状	70	535	408
30	Co 15%	0.1～2	20.7	球状	100	478	384
31	Co 15%	0.1～2	30.5	球状	0	466	336
32	Co 15%	0.1～2	30.5	球状	5	565	383
33	Co 15%	0.1～2	30.5	球状	20	588	396
34	Co 15%	0.1～2	30.5	球状	50	544	341
35	Co 15%	0.1～2	30.5	球状	70	475	314
36	Co 15%	0.1～2	30.5	球状	100	424	296

[0098]

[Table 3]

電池	置換元素種	一次粒子径 (μm)	二次粒子径 (μm)	二次粒子形状	微粉混合比率 (%)	放電容量 (mAh) 5サイクル	500サイクル
37	Mn 15%	0.1～2	5.3	球状	20	602	554
38	Cr 15%	0.1～2	5.4	球状	20	605	562
39	Fe 15%	0.1～2	4.9	球状	20	628	584
40	V 15%	0.1～2	5.5	球状	20	592	555
41	Al 15%	0.1～2	4.4	球状	20	572	554

[0099]

[Table 4]

電池	置換元素量	一次粒子径 (μm)	二次粒子径 (μm)	二次粒子形状	微粉混合比率 (%)	放電容量 (mAh) 5サイクル	500サイクル
42	Co 10% Mn 5%	0.1～2	6.3	球状	0	532	504
43	Co 10% Mn 5%	0.1～2	6.3	球状	5	583	552
44	Co 10% Mn 5%	0.1～2	6.3	球状	20	605	555
45	Co 10% Mn 5%	0.1～2	6.3	球状	50	596	557
46	Co 10% Mn 5%	0.1～2	6.3	球状	70	587	455
47	Co 10% Mn 5%	0.1～2	6.3	球状	100	448	360

[0100]

[Table 5]

電池	置換元素量	一次粒子径 (μm)	二次粒子径 (μm)	二次粒子形状	微粉混合比率 (%)	放電容量 (mAh) 5サイクル	500サイクル
48	Co 15%	0.1～2	6.04	球状	0	526	502
49	Co 15%	0.1～2	6.04	球状	5	611	571
50	Co 15%	0.1～2	6.04	球状	20	622	592
51	Co 15%	0.1～2	6.04	球状	50	594	560
52	Co 15%	0.1～2	6.04	球状	70	527	447
53	Co 15%	0.1～2	6.04	球状	100	431	355
54	Co 15%	0.1～2	6.04	球状	10	634	588

[0101]

[Table 6]

電池	置換元素量	一次粒子径 (μm)	二次粒子径 (μm)	二次粒子形状	微粉混合比率 (%)	放電容量 (mAh) 5サイクル	500サイクル
55	Co 15%	5.0	15.0	球状	20	458	426
56	Co 15%	15.0		塊状	20	375	286
57	Ni100%	1.0	6.0	球状	20	633	216

[0102]Although improvement in some discharge capacity is accepted by adding the minute-crystals grains obtained by grinding when the active material whose secondary particle diameter is smaller than 2 micrometers is used (cells 1-6), all discharge capacity is not small [as 500 or less mAh] more preferred than the test result (Table 2) of Embodiment 1.

[0103]This has a grain size of an aggregated particle as small as 2 micrometers or less, and it is because the effect filled up with the opening between grains was hardly acquired since there were no minute-crystals grains and difference which are added.

[0104]On the other hand, since the opening between aggregated particles is filled up with an active material and also an electronic conduction course is also secured, when secondary particle diameter adds the minute-crystals grains obtained by grinding by the not less than 2-micrometer cells 7-30, Also in 500-mA high rate discharge, the large discharge capacity of 550 or more mAh was obtained.

[0105]Since a conducting route was held to some extent even if an active material miniaturizes in connection with a charging and discharging cycle, since there are few openings between grains, the good cycle characteristic was acquired.

[0106]However, when secondary particle diameter was as large as 30 micrometers (cells 31-36), in early stages, big discharge capacity was secured, but in connection with the charging and discharging cycle, the aggregated

particle was destroyed, the active material was omitted from the electrode, and discharge capacity decreased remarkably.

[0107]Thus, as for the grain size of an aggregated particle, it is desirable that it is the unidirectional particle diameter of 20 micrometers or less in SEM observation.

[0108]Also in the case of Embodiments 2-6 by which the same effect taken in Embodiment 1 substituted some nickel with Mn, Cr, Fe, V, and aluminum (cells 37-41), it was obtained, and the good cycle characteristic was acquired with high capacity.

[0109]Even if one or more kinds of metal (for example, Embodiment 7 Co, Mn) substitutes some nickel, by the cells 43, 44, and 45 in the range of this invention, a good cycle characteristic is realizable with high capacity.

[0110]In this example, although only the case of the combination of Co and Mn was shown, when it was the combination of Co, Mn, Cr, Fe, V, and aluminum, it was checked that the same characteristics are obtained in every combination. The same effect was acquired even if it combined three or more kinds of metal.

[0111]As the cells 49, 50, and 51 of Embodiment 8 showed, after grinding some nickel hydroxide which is a raw material beforehand, it mixes with an unground thing, the effect of this invention is mixed with lithium salt after that, and when a lithium multiple oxide is compounded, the same effect is completely acquired.

[0112]Although the ball mill was used as the grinding method of an aggregated particle in this invention, even if it uses the grinders (for example, a pebble mill, a vibration mill, a jet mill, etc.) generally applied, it cannot be overemphasized that the same effect is acquired.

[0113]As Embodiment 9 showed, after constituting an active material on a charge collector beforehand, even if it ground the aggregated particle by rolling with a roller press, the same effect was acquired as the cell 54 showed.

[0114]On the other hand, like the cell 55 shown according to the comparative example 1, since the effect filled up with an opening is hardly acquired even if primary particle diameter mixes 5 micrometers and a large thing with an aggregated particle, early discharge capacity falls remarkably.

[0115]For this reason, as for primary particle diameter, it is desirable that it is 2 micrometers or less. When massive grains were used, restoration nature was low as it was, and when this massive grain was ground further, discharge capacity fell extremely like the cell 56 of the comparative example 2. The crystal structure of the grain interface by which this was destroyed by grinding was destroyed, and it was considered as a cause that movement of a lithium ion is checked.

[0116]thus -- positive active material is an aggregated particle in the range whose unidirectional particle diameter (Feretdiameter) in which many minute grain children gather is 2-20 micrometers -- spherical or an ellipse -- a spherical thing is desirable.

[0117]Although early capacity was large like the cell 57 of the comparative example 3 in the case of the $LiNiO_2$ haplophase which does not use substitution metal, extreme cycle degradation was accepted.

[0118]Crystal structure changes in connection with charge and discharge, and this is considered to be the thing in which reversibility was lost.

[0119]Thus, it is $LiNi_xM_{1-x}O_2$ () as this invention showed. [M] [Co and] Any one or more kinds of Mn, Cr, Fe, V, and aluminum and x:1>x>=0.5 are used as positive active material, The minute grain child who has this positive active material in the range whose unidirectional particle diameter (Feret diameter) in SEM observation is 0.1-2 micrometers, Only when it is a mixture of the aggregated particle in the range whose unidirectional particle diameter (Feretdiameter) in which many minute-crystals grains gather is 2-20 micrometers, a cell with a good cycle characteristic can be realized with such high capacity.

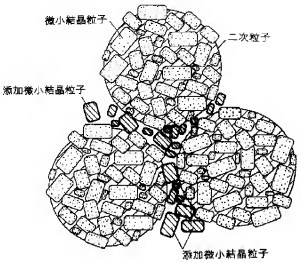
[0120]Although sulfate was used as a salt which adds substitution metal in this invention, otherwise, the effect that nitrate, and a chloride and acetate are also the same is acquired.

[0121]Although sodium hydroxide was used as an alkali source which deposits a hydroxide, the same effect is

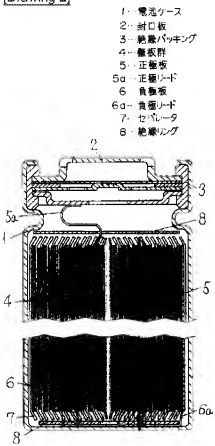
acquired even if it uses lithium hydroxide and potassium hydroxide.
[0122]Although it evaluated using the cylindrical cell in the above-mentioned embodiment, the same effect is acquired even if cell shape, such as a square shape, differs.
[0123]although the carbonaceous material was used for the anode in the above-mentioned embodiment, in order that the effect in this invention may act in a cathode board, the same effect is acquired even if it uses other negative electrode materials, such as oxides, such as a lithium metal, a lithium alloy, Fe_2O_3, WO_2, WO_3.
[0124]moreover -- although lithium hexafluorophosphate was used as an electrolyte in the above-mentioned embodiment -- other lithium content salt, for example, lithium perchlorate, tetrafluoride lithium borate, and lithium trifluoromethanesulfonate and hexafluoride -- arsenic acid -- the effect that lithium was also the same was acquired.
[0125]Although ethylene carbonate and the mixed solvent of ethyl carbonate methyl were used in the above-mentioned embodiment, The same effect was acquired even if it used nonaqueous solvents and these plural system mixed solvents, such as chain ester, such as chain ether, such as cyclic ether, such as cyclic ester, such as other nonaqueous solvents, for example, propylene carbonate etc., and tetrahydrofuran, and dimethoxyethane, and methyl propionate.
[0126]
[Effect of the Invention]At this invention, it is $LiNi_xM_{1-x}O_2$ () so that clearly from the above explanation. [M] [Co and] They are one or more kinds chosen from among Mn, Cr, Fe, V, and aluminum, x: The nonaqueous electrolyte secondary battery which excelled [high capacity] in the cycle characteristic can be provided by using 1> x>=0.5 as positive active material, specifying the minute-crystals grains of this active material, the grain size of the aggregated particle in which much these gathered, and particle shape, and using the cathode board which used these by the mixed state.

[Brief Description of the Drawings]
[Drawing 1]The key map of this invention
[Drawing 2]The longitudinal section of a cylindrical cell
[Explanations of letters or numerals]
1 Cell case
2 Obturation board
3 Insulating packing
4 Group of electrode
5 Cathode board
5a positive electrode lead
6 Negative electrode plate
6a negative electrode lead
7 Separator
8 Insulating ring

[Drawing 1]



[Drawing 2]



[Translation done.]